MOLECULAR ORBITAL THEORY AND THE REACTIVITY OF POLYPHENYLS

By SADHAN BASU
INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA-32.

(*Received for publication, April 6, 1954*)

ABSTRACT—Resonance energies, electronic transitions and π-electron densities have been calculated by LCAO MO method for polyphenyls. The electron densities have been correlated with the chemical reactivities of these compounds at different positions of the ring. Possibility of using frontier electron density instead of π-electron density has also been indicated.

INTRODUCTION

Many properties of unsaturated organic molecules may be, at least qualitatively correlated with the distribution of electron densities in the isolated molecule. Such properties include the case of cationoid substitution at different positions of the molecule. Extensive work has already been done in this field by Huckel (1931), Pauling *et al* (1953), Coulson (1947) and others for a large number of aliphatic, aromatic and hetero-cyclic conjugated organic molecules. In the present paper is reported the results of molecular orbital calculations for three polyphenyls, namely, biphenyl, terphenyl and tetraphenyl. The chemistry of biphenyl is fairly well established and a correlation of the reactivity of this compound with π-electron density has been made. The chemistry of two other compounds are not yet fully established. A prediction of their reactivity from theoretical calculation will constitute a test of the validity of such calculation as the chemistry of these compounds are investigated.

Application of molecular orbital theory to these system is expected to be rather unjust. The C—C bond distance between two benzene ringe is greater than those in the ring itself ; consequently a complete overlap of the π-electron wave function cannot be freely assumed. However, recent application of electron gas theory to the spectra of these compounds by Nakajima (1953) and its fair agreement with experimental result show that the concept of complete overlap of the wave function is approximately correct. Furthermore such overlaping will be possible if the rings lie on the same plane ; but if they take up a mlutiplaner configuration the interaction between various rings will be destroyed and the system will behave like a collection of benzene rings. But since in co-planer configuration resonance effect will reduce the energy of the system appreciably, this configuration

will be most favoured in the ground state, although in the excited state multiplaner configuration will be possible.

THEORETICAL FOUNDATION

The method of calculation is well known. It is assumed that in the conjugated system the greater reactivity may be attributed to π-electrons and not σ-electrons. Attention will therefore be restricted to the former. It is convenient to express the molecular orbitals (MO) of the π-electrons as linear combination of atomic orbitals (LCAO) of the carbon atoms constituting the conjugated system. Each MO is then written in the form

$$\psi = \sum_r C_r \phi_r \qquad \ldots (1)$$

where ϕ_1 to ϕ_r are the $2p_z$ atomic orbitals of the carbon atoms 1 to r in the system constituting r atoms in conjugation. It is further assumed that the atomic orbitals (AO) are orthogonal and normalized, *viz.*

$$\int \phi_r \phi_s d\tau = 1, \text{ if } r = s$$
$$= 0, \text{ otherwise} \qquad \ldots (2)$$

On these assumptions, the energy of an electron (E) in ψ is given by the usual secular equations

$$(E_r - E) C_r + \sum \beta_{rs} C_s = 0$$
$$s \neq r, \ (r = 1, 2, 3 \ldots r) \qquad \ldots (3)$$

where
$$\left.\begin{aligned} E_r &= \int \phi_r H \phi_r d\tau = \text{Coulomb integral} \\ \beta_{rs} &= \int \phi_r H \phi_s d\tau = \text{resonance integral} \end{aligned}\right\} \qquad \ldots (4)$$

In solving these equations for the molecules under consideration we assume that

$$\beta_{rs} = \begin{cases} \beta, \text{ if } r \text{ and } s \text{ are bonded} \\ 0, \text{ otherwise} \end{cases} \qquad \ldots (5)$$

where β has the same value for all C – C bonds. We assume also that the Coulomb integral E_r has got the same value for all the carbon atoms and write it as E_0.

With these assumptions, the secular equation (3) takes the form

$$(E_0 - E) C_r + \sum_{s \text{ bonded to } r} \beta C_s = 0$$

Or more briefly

$$W C_r + \sum \beta C_s = 0 \qquad \ldots (6)$$

It is evident from equation (6) that for simplest case of biphenyl with 12 carbon atoms in conjugation, we get 12 secular equations from which we can construct a 12×12 determinant in W and β, the solution of which will give us 12 roots for W and consequently for E the energy states of the π-electrons. Each of these energy states will be occupied by two electrons of opposite spin ; so in the ground state lower 6 of 12 energy states will be occupied. Substituting these roots in the secular equation (6) and applying

the condition that $C_1^2+C_2^2+\ldots C_{12}^2=0$, the coefficients C_1, C_2, C_3, etc. for various energy states can be calculated. The total density of π-electrons at, say atom 5, is given by $2\sum C_5^2$ where the summation is taken over all the occupied orbitals.

APPLICATION OF GROUP THEORY

From what has been said it is clear that in order to get energy states of the π-electrons we are faced with the solution of a 12 order equation in the case of biphenyl, 18 order equation in terphenyl and 24 order equation in tetraphenyl. Difficulties, labour and uncertainties associated with such calculations are well known. However, the symmetric structure of many organic molecules enables us to break up these higher order equations into a number of lower order ones by applying the group theory. We will illustrate the method by taking the case of biphenyl.

The symmetry group in biphenyl is D_{2h} and π-electron molecular orbitals are of species B_{1u}, B_{2g}, B_{3g} and A_u. The numbering of atomic orbitals are shown in figure 1.

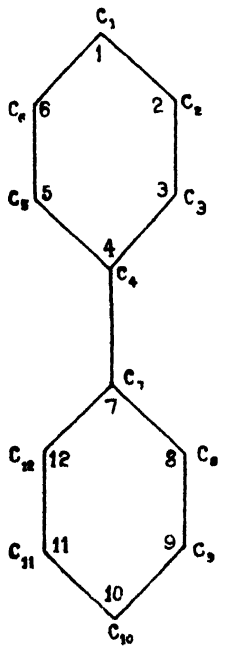

FIG. 1.
AO forming the MO for biphenyl.

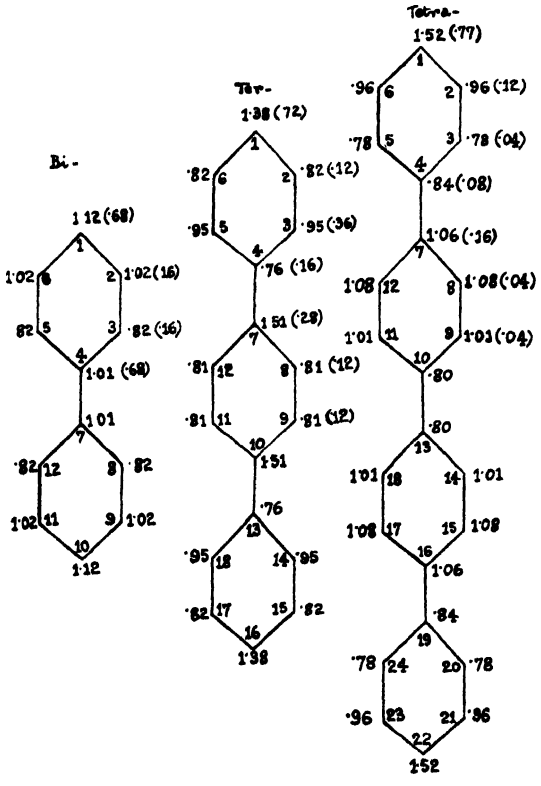

FIG. 2.
Total π-electron density at different carbon atoms (number within parenthesis indicate frontier electron density).

We then have for MO species

B_{1u} : $C_2=C_6=C_9=C_{11}$, $C_3=C_5=C_8=C_{12}=$, $C_1=C_{10}$ and $C_4=C_7$.

B_{2g} : $C_2=C_6=-C_9=-C_{11}$, $C_3=C_5=-C_8=-C_{12}$, $C_1=-C_{10}$ and $C_4=-C_7$.

B_{3g} : $C_2=-C_6=C_9=-C_{11}$, $C_3=-C_5=C_8=-C_{12}$, and

$$C_1=C_4=C_7=C_{10}=0$$

and A_u : $C_2=-C_6=-C_9=C_{11}$, $C_3=-C_5=-C_8=C_{12}$ and

$$C_1=C_4=C_7=C_{10}=0$$

Applying these conditions to equation (6) we can break up the original 12 order determinant into two fourth order and two second order equations, the solution of which gives us the values for twelve energy states out of which lower six will be occupied in the ground state. The equations were solved by 'pinch' method correct up to first decimal place.

The calculated electron densities are shown in the figure 2 for three polyphenyls. Values are necessarily approximate.

Resonance energies : Total single electron energy in the occupied states for biphenyl is $6E_0+8.4\beta$ and since each energy state is occupied by 2 electrons the total π-electron energy is $12E_0+16.8\beta$. For two Kekule strutures of the biphenyl with fixed bonds we have the total π-electron energy $12E_0+12\beta$. So the resonance or delocalisation energy of biphenyl is $(12E_0+16.8\beta)-(12E_0+12\beta)=3.8\beta$. Similarly for ter- and tetraphenyl the calculated resonance energies are 6.36β and 9.40β respectively. It is evident therefore that the energies are increasingly lower with increase in the number of phenyl rings.

Absorption spectra : The first intense absorption line in the UV region takes place due to a transition of the π-electron from the highest filled level to the lowest vacant level ($N\rightarrow V$ transition). For biphenyl this transition corresponds to an energy change of β. If we assume this to be equal to the centre of gravity of the UV line (39,2000 cm^{-1}) in biphenyl, then the value of β comes out to be 19,000 cm^{-1}. (For simple benzene system $\beta=23{,}000$ cm^{-1} (Nakajime, 1953.) With this value of β we calculate the value of the centre of gravity of the absorption line for ter-and tetraphenyl from the corresponding energy changes (1.6β and 1.35β respectively) in $N\rightarrow V$ transition. The calculated values for ter- and tetraphenyl are respectivly 31,560cm^{-1} and 26,460cm^{-1} compared to the experimental values of 35,000cm^{-1} and 32,700cm^{-1}. Although the absolute values do not agree closely enough, the shift in the absorption frequencies are in the right direction, namely, towards red region (the familiar red-shift in reasonating molecules). This dis-agreement, however, is not surprising. The experimental values are for solutions of these compounds in some organic solvent, while the theoretical values are true for crystalline solid where the molecule takes up a coplaner structure as established by X-ray investigation (Dhar, 1932). Measurement of UV spectra will therefore constitute a real test of the theory when applied to crystalline solid.

π-Electron density and chemical reactivity : The problem of predicting the reactivity of organic molecule at a particular position has been solved to some extent by means of LCAO molecular orbital method. In treating such problems, two methods have been used by several authors: one may be called the 'transition state' method (Wheland, 1942) and the other 'π-electron density' method (Pauling, 1935). In the former method the configuration of transition complex is assumed *a priori* on the basis of some other theoretical or empirical arguments, and the method is usually associated with tedius calculations. In the latter method, on the other hand, the density of π-electron at variours positions are calculated as has been done in the present case (figure 2). Next, it is assumed that the greater the calculated π-electron density at one position, the greater the ease and rate of substitution at that position by cationoid reagent, while anionoid substitution proceeds most readily at the position where the calculated density is lowest. In biphenyl position of highest electron densities are 1 and 10. So it gives 1 : 10 dinitro, dibromo, dichlcro and disulfonated products. Next in order of reactivity are the position 4 and 7. These positions are sterically hindered and an attack at these positions brings about the degradation of the molecule leading to the formation of benzoic acid. With boiling nitric acid, however, biphenyl gives 1 : 3 and 10 : 8 dinitro derivatives. This is similar to ortho-para substitution in benzene. Consequently we may assume that under this condition biphenyl takes up a multiplaner configuration. Similar is the case of oxidation with ozone when a tetraquinone is formed. That the ring system takes up a multiplaner configuration in these compounds has been established by their optical activity (Gilman, 1947).

In the case of terphenyl the electron densities are maximum at 7 and 10 position. Consequently this compound will undergo easy oxidation to benzoic acid, but will never form terepthalic acid. Next in order of reactivity are the positions 1 and 16, which will give diderivatives fairly easily. Central ring in this compound will be least reactive and the compound will decompose before any substitution can enter the central ring.

Tetraphenyl will be more stable than terphenyl, electron density being maximum at 1 and 22 position. Further more substitution will enter the terminal rings leaving the central rings unaffected. Degradation of this compound will lead to formation of benzoic acid but not dibenzoic acid.

All these predictions are valid for co planer configuration. With hot nitric acid reaction may take different course due to multiplaner configuration of the molecule.

Frontier electron density and reactivity : From what has been said above it is clear that the π-electron density qualitatively predicts the reactivity of different positions of biphenyl towards various reagents, When we try to make a semi-quantitative calculation of the percent yield of a product we are faced with some difficulties. Thus if M be the sum of π-electron densities at different positions and N the π-electron

density at the position, say 1, then the percent yield of, say nitrated product with substitution at 1 and 2 for biphenyl should be respectively 30.9 and 13.2. But in actual practice no product with substitution at 2 position is obtained. Such discrepancies have also been noticed in the case of spiro-hydrocarbons. In order to get around these difficulties Fukui *et al* (1953) introduced the concept of frontier electron density method in predicting the reactivity of conjugated compounds. They assumed that in a chemical reaction the electron at the top of the filled energy level enters into reaction, i. e. the electrons at the top has got some kind of valency character. So they assumed that it is the density of frontier electron that will govern the actual extent of reaction. Such calculations have given encouraging result for spiro-hydrocarbons. The results of frontier electron density calculation for polyphenyls are also shown in figure 2 (within paranthesis). It will be evident that the frontier electron density at 2, 3, 5 and 6 positions are all equal and the percent yield of monosubstituted product at 1 and at any other position are respectively 34 and 8. Although frontier electron density method improves the result, still it is far from being quantitative. Further it is not clear why frontier electrons should govern the extent of reaction, because the course of reaction is controlled by the attractive force between the approaching redical or ion and the particular position of the molcule. This evidently will depend on the total π-electron density. It may, however, be argued that although the point of maximum attack will be governed by the total π-electron density, the extent to which the reaction will proceed may be governed by the frontier electron density. How far these assumptions are justified will become clear as more and more frontier electron density calculations are made and compared with experimental results.

ACKNOWLEDGEMENT

Thanks are due to Dr. P. C. Dutt. and Mr. P. N. Bagchi for helpful discussions.

REFERENCES

Coulson, C., 1947, *Trans Farad. Soc*, **43**, 87.
Dhar, J., 1932, *Ind J. Phys* **7**, 43.
Fukui, K., Tenezawa, T. and Shingu, H. 1952, *J. Chem. Phys.*, **20**. 722.
Gilman, H., 1947, Organic Chemistry, an advanced treatise, Vol. I,
Huckel, E., 1931, *Z. Physik.*, **70**, 204.
Nakajima, T., 1953, *Sci. Rep. Res. Instt., Tohoku Univer.*, **5**, 98.
Pauling, L. and Wheland, G. ,1933, *J. Chem. Phys.*, **1**, 362.
Pauling, L. and Wheland, G., 1935, *J. Amer. Chem. Soc.*, **57**, 2086.
Wheland, G., 1942 *ibid.*, **64**, 900